Short communication

Suppression of aluminum corrosion by using high concentration LiTFSI electrolyte

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HIGHLIGHTS

► In higher LiTFSI concentration, aluminum corrosion was remarkably suppressed.
► From XPS depth profile, Li and F are mainly detected unlike normal concentration.
► We found a film composed of LiF played a role to prevent from aluminum corrosion.
► As results, a battery with high LiTFSI concentration could work without degradation.

ARTICLE INFO

ABSTRACT

Although lithium bis(trifluoromethanesulfonyl imide) (LiTFSI) has a high thermal stability and fine tolerance to water and is an outstanding candidate as an electrolyte, there is an urgent need to control aluminum corrosion. Here, we explain how we suppressed aluminum corrosion by controlling the LiTFSI concentration. SEM observations and XPS depth profiles of the electrode at high LiTFSI electrolyte concentrations showed that stable passivation film composed of LiF was formed on an aluminum electrode, which prevented the continuous decomposition reaction of the LiTFSI electrolyte. As a result, a lithium-ion battery with LiTFSI demonstrated excellent properties for several cycles without aluminum corrosion, which should accelerate progress in its applications to industry.

1. Introduction

Lithium-ion batteries (LIBs), with their high energy density and long lifetimes, have been attracting attention in recent years due to their wide potential applications in electric vehicles and large-scale stationary battery systems [1–3]. Lengthening the battery lifetime is currently one of the most important issues in these applications because a longer lifetime results in lower costs for the users.

In order to lengthen the lifetime, it is absolutely essential to reduce deterioration in LIBs. Hydrogen fluoride (HF) formed from the dissociation reaction of $LiPF_6$ and impurities such as water during charge-discharge is a primary factor in LIB deterioration [4–6]. HF can lead to unwanted side reactions such as the Mn^{2+} dissolution process. This reaction also causes the deposition of Mn^{2+} on the anode and disrupts the intercalation process in LIBs. Therefore, the use of electrolytes that are highly stable against water is a promising strategy toward achieving LIBs with longer lifetimes.

Lithium bis(trifluoromethanesulfonyl imide) (LiTFSI) has recently attracted attention as an alternative lithium salt to $LiPF_6$, in part due to its high stability against water [7–9]. However, an aluminum electrode used as a positive electrode current collector corroded around 3.8 V vs. Li/Li^+ when the LiTFSI electrolyte was contained in LIBs [10–12].

Several researchers have already reported the suppression of aluminum corrosion and have succeeded in improving the performance of batteries [13–15]. Kanamura et al. reported that passive film consisting of AlOF and AlF_3 could be formed on aluminum surfaces by adding a small amount of HF to an LIB that had an LiTFSI electrolyte [16]. However, the passivation film was gradually destroyed within several cycles. Morita et al. also reported that aluminum corrosion could temporarily be suppressed by adding

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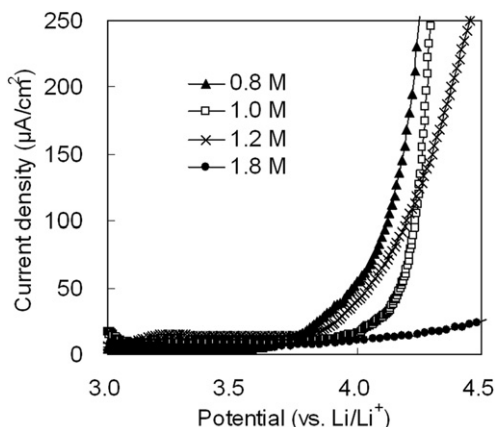 *E-mail address:* k-matsumoto@dx.jp.nec.com (K. Matsumoto).

Fig. 1. Linear sweep voltammetry (LSV) on an aluminum electrode (2.0 × 3.0 mm) in EC: DEC mixed electrolyte containing different LiTFSI concentrations with a scan rate of 1.0 mV s^{-1}.
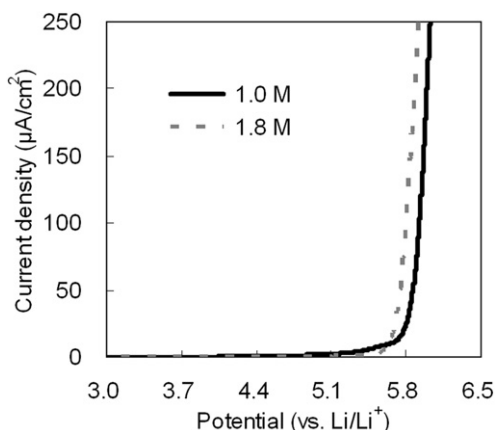

Fig. 2. LSV on a platinum electrode ($\varphi = 3$ mm) in EC: DEC mixed electrolyte containing different LiTFSI concentrations with a scan rate of 1.0 mV s^{-1}.

LiPF$_6$, although they determined that the effect of this suppression was insufficient to improve the potential stability of aluminum because the passivation film was thinner than the electrolyte that only contained LiPF$_6$ [17].

In the current study, we found that the extent of corrosion on an aluminum electrode strongly depended on the concentration of LiTFSI and that the suppression of corrosion was closely related to the surface morphology of aluminum when voltage was applied. We also discovered that a battery with a high concentration of LITFSI electrolyte enabled stable charge-discharge cycles without corrosion.

2. Experiment

Linear sweep voltammetry (LSV) was measured to determine the starting potential of aluminum corrosion. Electrochemical cells were assembled with an LiTFSI/EC: DEC (3: 7 by volume) electrolyte. Aluminum or platinum (working electrode) and lithium (reference and counter electrodes) were used in the three-electrode cell. The concentration of LiTFSI was adjusted to create 0.8, 1.0, 1.2, and 1.8 mol L^{-1} (M) in mixed solvents EC: DEC (3: 7 by volume). Potential was applied to the cell from 3.0 to 4.5 V vs. Li/Li$^+$ for the aluminum electrode and from 3.0 V to 6.5 V vs. Li/Li$^+$ for the platinum electrode. The EC, DEC, and LiTFSI used in these measurements were purchased from Ube Kosan Co. Ltd., and the pure aluminum foil and lithium foil were purchased from Honjo Kinzoku Kogyo Co. Ltd. Results of Karl Fischer titration showed that the water content in the mixed electrolytes was less than 15 ppm.

The difference in the surface morphology of the aluminum electrode between high and low LiTFSI concentration in the electrolyte was investigated by scanning electron microscopy (SEM, Hitachi S-4800). The aluminum electrodes were prepared by washing them with DEC and drying them at 25 °C for 1 h after they were removed from the three-electrode cell under an inert atmosphere. Analyses were performed on the surface of the aluminum side facing the lithium electrode after potential from 3.0 V to 4.3 V vs. Li/Li$^+$ was applied at 0.5 mV s^{-1} and maintained at the potential of 4.3 V vs. Li/Li$^+$ for 3 h.

The component of the surface layer in the electrolyte containing each concentration was investigated by X-ray photospectroscopy (XPS) with an Al-Kα monochromatic X-ray excitation source (ULVAC-PHI Quantera SXM). The area analyzed on each sample was 100 μm in diameter. The depth profiles were measured by sputter etching using an Ar+ ion beam. The sputter rate was 5.6 nm min^{-1} (conversion at SiO$_2$) and the measurement interval was 1 min.

Cycle tests were performed using coin cells sealed in a dry-air room. A LiMn$_2$O$_4$ electrode was assembled in the coin cell with lithium metal as the counter electrode separated by a propylene separator (Celgard #2500). Charge and discharge evaluations at 0.2 C rates were conducted in these cells from 3.0 to 4.3 V in several cycles.
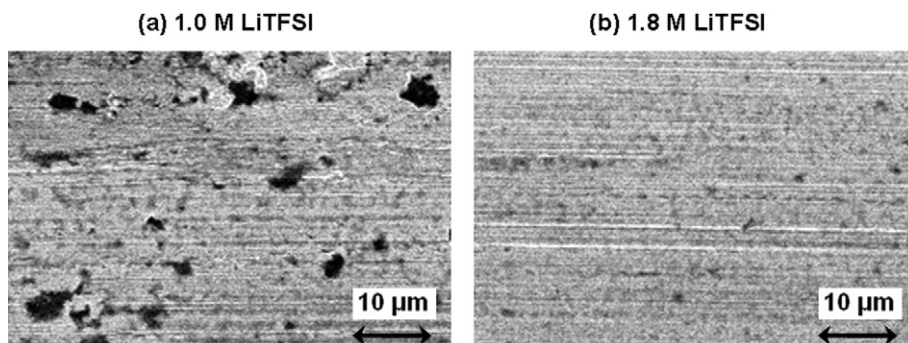
(a) 1.0 M LiTFSI   **(b) 1.8 M LiTFSI**

Fig. 3. SEM images of aluminum surface in (a) 1.0 M LiTFSI and (b) 1.8 M LiTFSI after applying potential.
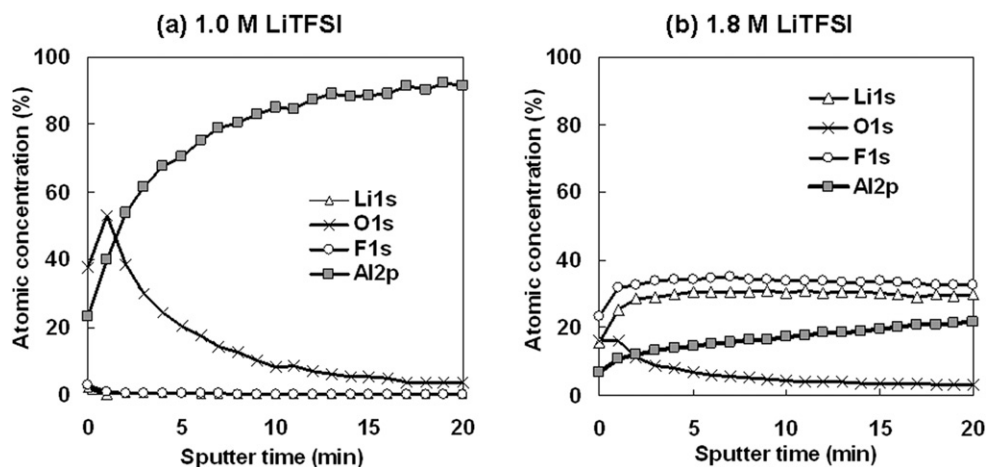
Fig. 4. XPS depth profiles of aluminum electrode after LSV. (a) 1.0 M LiTFSI and (b) 1.8 M LiTFSI dissolved electrolyte.
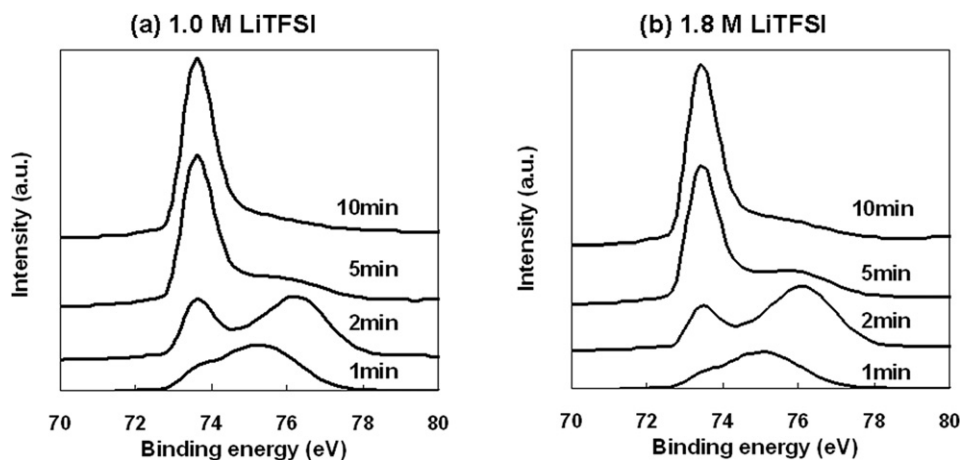

Fig. 5. Al2p XPS core peak on aluminum after LSV in (a) 1.0 M LiTFSI and (b) 1.8 M LiTFSI dissolved electrolyte.

3. Results and discussion

The dependence of LiTFSI concentration on the LSV current with an aluminum electrode is shown in Fig. 1. The aluminum electrode was oxidized immediately from about 3.7 V to 4.0 V vs. Li/Li$^+$ at the 0.8, 1.0, and 1.2 M LiTFSI concentrations. The increase in current caused by oxidizing the aluminum electrode implies aluminum corrosion [11]. However, at a higher concentration such as 1.8 M LiTFSI, the anodic current was very small until 4.5 V vs. Li/Li$^+$. In the second scan, the anodic current was less than the first one (figure
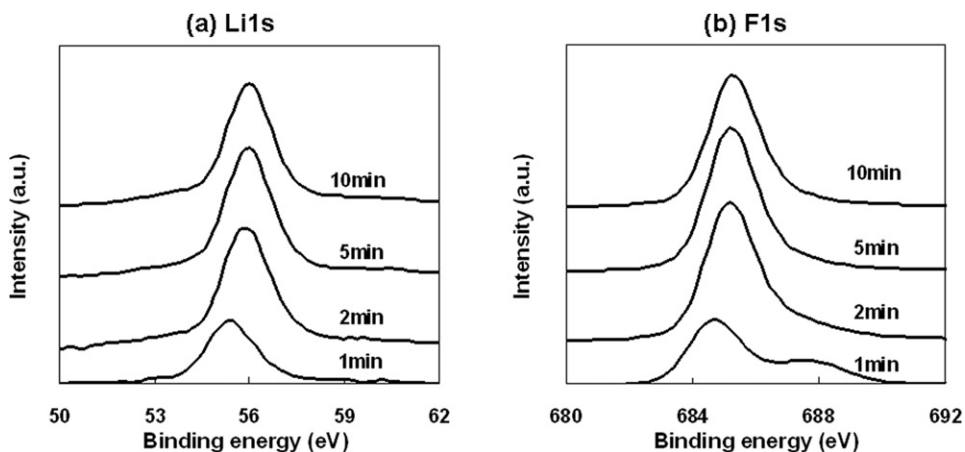

Fig. 6. (a) Li1s and (b) F1s XPS core peak on aluminum electrode after LSV in 1.8 M LiTFSI dissolved electrolyte.
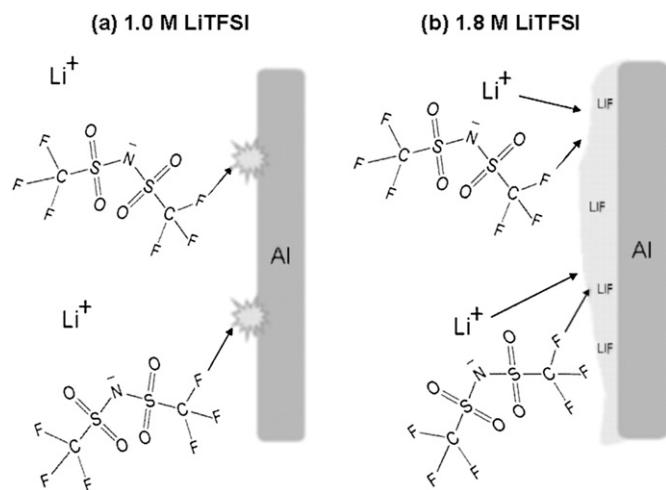
Fig. 7. Mechanism for LiTFSI decomposition and formation of LiF film in (a) 1.0 M LiTFSI and (b) 1.8 M LiTFSI.

not shown). This means that the aluminum corrosion does not occur in such a higher LiTFSI concentration electrolyte. We found that the corrosion reaction on the aluminum electrode was suppressed for higher LiTFSI concentrations. In addition, results of the LSV measurement under the same conditions apart from the working electrode of platinum (Fig. 2) showed that the starting potential of the current increase on the platinum electrode did not depend on the LiTFSI concentration at all. This is interesting because we had expected that on the aluminum electrode a passivation film was formed when potential was applied in the higher LiTFSI concentration and that this film would suppress aluminum corrosion. To determine if the film really was a passivation film, we carried out SEM observations and XPS measurements on the aluminum surface after applying the potential at different LiTFSI concentrations.

SEM observations of the surface morphology of an aluminum electrode after applying potential at 1.0 and 1.8 M LiTFSI concentrations (Fig. 3) differed considerably in the change of current related to electrochemical oxidation (Fig. 1).

Some pitting could be seen on the surface in 1.0 M LiTFSI/EC: DEC. The aluminum electrode was pitted by the corrosion reaction reported by Zhang et al. [13]. However, we found that pitting did not occur or that it was very small in 1.8 M LiTFSI/EC: DEC. This

indicates that aluminum corrosion rarely occurred at high LiTFSI concentrations.

The XPS depth profile shows the components of deposition film on aluminum after applying potential (Fig. 4). Al and O atoms were dominant in 1.0 M LiTFSI/EC: DEC (Fig. 4(a)), and there were very few Li and F atoms on the aluminum electrode. In addition, the Al atom concentration increased with sputter time. Continued sputtering exposed pure aluminum because the oxide film of aluminum was removed (film thickness: approximately $\leqq 20$ nm). However, Li and F atoms were mainly detected instead of O and Al atoms in 1.8 M LiTFSI/EC: DEC. The atomic concentrations of Li and F were also almost the same and were constant during sputtering. Therefore, a thick deposition film composed of Li and F atoms on aluminum formed in 1.8 M LiTFSI.

Fig. 5 shows the XPS spectra of Al 2p for the aluminum surface after applying potential. The peaks at 74.8 eV, 75.9 eV, and 74.0 eV were respectively assigned to Al_2O_3, AlF_3, and Al. From these results, in both low and high LiTFSI concentration electrolytes, it can be seen that Al_2O_3 and AlF_3 formed on the surface of aluminum electrode (Fig. 5), which is in agreement with the results for the LiPF$_6$ electrolyte [17]. However, these materials were not effective as passivation film because aluminum corrosion was observed in the 1.0 M LiTFSI electrolyte. The XPS spectra of Li1s and F1s were only detected in 1.8 M LiTFSI/EC: DEC, and their peaks were attributed to LiF (Fig. 6). The peak intensity did not change during sputter times of 10 min. These results indicate that a thick film (more than 110 nm) composed of LiF was formed on the aluminum electrode. We therefore concluded that the corrosion reaction of the aluminum electrode when potential was applied was hindered by the formation of LiF film at a higher LiTFSI concentration. For this reason, the anodic current in the LSV measurement was very small.

Here, we discuss why the formation of passivation film depended strongly on the concentration of the LiTFSI electrolyte. As described above, at a lower concentration the thin film composed of AlF_3 and Al_2O_3 was formed on the aluminum surface when potential was applied. At a higher concentration, on the other hand, thick film composed of LiF was formed. This difference seems to come from the dissociation of lithium salt, which is influenced by the concentration [18]. Therefore, we conclude the film formation process on the aluminum surface when potential was applied occurred as follows (Fig. 7). At low concentrations, lithium salt was mostly separated into a lithium cation and TFSI anion, with both ions remaining separated in the electrolyte. When potential was applied, the TFSI anion was oxidatively decomposed on the aluminum and the fluoride anion (F$^-$) was
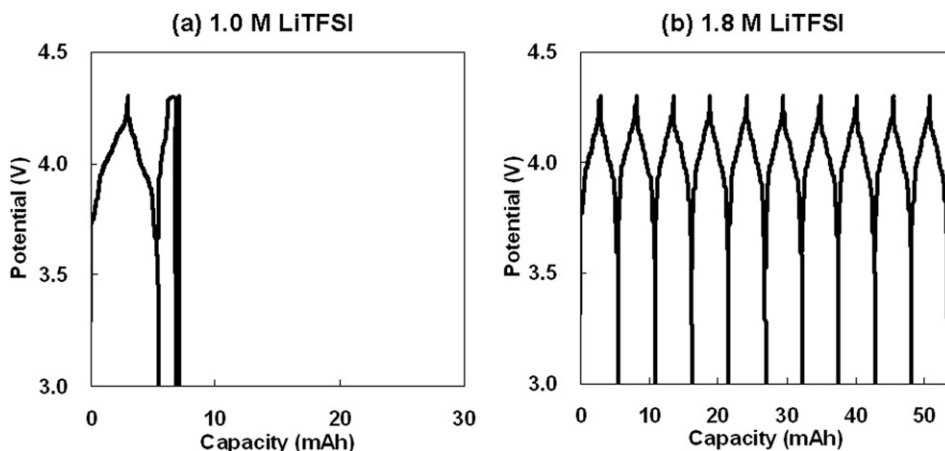

Fig. 8. Charge–discharge curve of Li/EC: DEC. (a) 1.0 M LiTFSI and (b) 1.8 M LiTFSI/LiMn$_2$O$_4$ at 0.2 C rate.

generated (this is supported by the result reported by Krause et al. [11]). F⁻ then easily connected with an aluminum cation instead of a lithium cation since the lithium cation stayed away from F⁻ (Fig. 7(a)). At higher LiTFSI concentrations, on the other hand, the dissociation constant of lithium salt must have been small, and the lithium salt had difficulty separating into lithium cation and TFSI anion. Therefore, the lithium cation and F⁻ generated by TFSI oxidative decomposition stayed comparatively close to each other when potential was applied, resulting in the formation of LiF (Fig. 7(b)).

More research is needed to identify which of these possible reasons played the main role in our results. Future work will likely include Raman spectroscopy or NMR measurements to investigate the degree of dissociation at several lithium salt concentrations.

The cycle tests were investigated with coin cells using 1.0 M and 1.8 M LiTFSI electrolytes (Fig. 8). The same capacity was obtained in the first cycle regardless of LiTFSI concentration. However, the discharge capacity in the second cycle was very small due to the corrosion reaction in 1.0 M LiTFSI/EC: DEC. As a result, further cycling became difficult. However, the charge and discharge capacity was constant in 1.8 M LiTFSI without any degradation during cycles, which indicates the possibility of lithium-ion batteries that can operate for a long time. Moreover, it should be noted that we succeeded in operating a lithium-ion battery using only an LiTFSI electrolyte.

4. Conclusion

Although LiTFSI has a higher thermal stability than $LiPF_6$ and is stable against water, aluminum corrosion occurred at 3.8 V vs. Li/Li^+. For this reason, the performance of a lithium-ion battery with LiTFSI worsened as cycles progressed. In response to this problem, we developed an easy way of dissolving LiTFSI at high concentrations to suppress aluminum corrosion. An XPS depth profile indicated that, unlike with a normal LiTFSI concentration, passivation film composed of LiF was formed on aluminum to prevent aluminum corrosion after potential was applied at higher LiTFSI concentrations. The difference in film components at different concentrations can possibly be attributed to the distance between the lithium cation and TFSI anion in the electrolyte. At higher LiTFSI concentrations, it seemed to be easier to connect the lithium cation and fluoride anion generated from the oxidation of TFSI because the dissociation of lithium salt rarely occurred and these ions were comparably close to each other. This suggests that a battery with high LiTFSI concentration could operate without aluminum corrosion.

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